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TECHNICAL NOTE

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COMPARATIVE STRENGTHS OF SOME ADHESIVE-ADHEREND SYSTEMS

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SUMMARY

The strength properties of various adhesive-adherend combination were determined as one phase of an investigation of the nature of adhesion. The adhesives were polyvinyl acetate, cellulose nitrate, resorcinol resin, casein, gum arabic, natural rubber, and neoprene. The adherends were stainless steel, aluminum alloy, paper-phenolic laminate, glass, birch wood, and hard rubber. The properties studied were double-lap shear, tensile, long-time loading shear, and impact strengths.

The tensile-adhesion and shear strength values for a given adhesive-adherend combination did not differ greatly except for wood and paper-phenolic laminate, which are nonisotropic. The highest values (up to 3600 lb/sq in.) were obtained with polyvinyl acetate and cellulose nitrate adhesives.

The thermosetting resorcinol resin showed no appreciable flow in supporting a load of 680 pounds per square inch for 6 months, whereas the thermoplastic polyvinyl acetate failed in 45 days under a load of 200 pounds per square inch.

The rubber-type adhesives which were weak compared with the other adhesives in the static load tests were definitely superior in the impact tests.

Better correlation of shear strengths was observed with the moduli of elasticity than with the dielectric constants of the materials used in the various adhesive-adherend combinations.

INTRODUCTION

Experimental work on adhesives has been concerned largely with the development and use of products for industrial purposes. The aircraft industry has employed adhesives quite extensively (references 1 to 5). Current interest in sandwich construction also serves to emphasize the increasing importance of adhesives in new types of airplanes.

Study of the fundamentals of adhesion has been relatively meager (references 6 and 7). A survey of the information available on the nature of adhesion was published recently by the National Advisory Committee for Aeronautics (reference 8).

An investigation, under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics, was undertaken at the National Bureau of Standards to obtain comparative data on the strengths of the bonds between various chemical types of adhesives and representative adherends. The results of these tests should give some indication of the specific attraction between these various materials and hence lead to a better understanding of the nature of adhesion.

The information will also be useful in the selection of adhesive-adherend systems for the more fundamental studies of adhesion which are in progress in this laboratory.

The courtesy of the Allegheny Ludlum Steel Company, Arabol Manufacturing Company, Carbide and Carbon Chemicals Corporation, Casein Company of America, E. I. du Pont de Nemours and Company, Inc., Hercules Powder Company, and Pennsylvania Coal Products Company in furnishing materials for use in this investigation is gratefully acknowledged.

DEFINITION OF TERMS

Shear strength

Maximum load sustained by the specimen divided by the bonded area. The bonded area for a double-lap-joint specimen is twice the product of the overlap and the width.

Tensile-adhesion strength

Maximum load sustained by the specimen divided by the bonded area

Statistical terms

Mean value

The arithmetic mean of a set of measurements

Standard error of the mean (usually called the "standard error" if no other statistic is referred to at the same time:

$$S.E. = \frac{r_1^2 + r_2^2 + r_3^2 + \dots + r_i^2 + \dots + r_n^2}{n(n-1)}$$

where

r_i difference between i th measurement and mean value

n number of measurements

Coefficient of variation (measures scattering as a percentage of the mean):

$$V = \frac{\frac{r_1^2 + r_2^2 + \dots + r_i^2 + \dots + r_n^2}{n-1}}{\text{Mean value}} 100$$

MATERIALS

The choice of adherends and adhesives for this work was governed by the desire to study many different chemical types of bonds. The adherends used included stainless steel, aluminum alloy, paper-phenolic laminate, plate glass, birch wood, and hard rubber. The types, sources, and thicknesses of these materials are listed in table I.

The types of adhesives used in this investigation are as follows:

Type	Adhesive
Cellulose ester	Cellulose nitrate
Thermoplastic resin	Polyvinyl acetate
Thermosetting resin	Resorcinol-formaldehyde
Protein	Casein
Vegetable	Gum arabic
Natural rubber	Rubber (smoked sheet)
Synthetic rubber	Neoprene

Compounding agents were used with the adhesives in as small amounts as possible in order to keep the chemical nature of the bond between adhesive and adherend of the simplest possible type. Camphor was added to the cellulose nitrate in order to bring its softening or flow temperature below its decomposition temperature. Thymol was added to

the gum-arabic solution as a preservative; otherwise the gum arabic became moldy. Neoprene and natural rubber were compounded with what was considered the minimum number of agents necessary to vulcanize them properly. Neither accelerators nor antioxidants were added. The types, sources, and formulation of the adhesives are shown in table II.

PREPARATION OF SPECIMENS

Surface Treatment of Adherends

The proper surface treatment of the adherend was found to be of primary importance in obtaining optimum bonds. Not only was the surface cleaned, but the freshness of the surface was preserved after cleaning by immersion in a solvent until the adhesive was applied.

The metals were cleaned in a volatile organic solvent to remove oil and grease and were pickled in acids to remove any oxide film. The stainless steel was treated with 50 percent aqua regia for approximately 5 seconds and rinsed thoroughly in cold water. The aluminum alloy was treated with a 5 percent phosphoric acid solution for about 5 minutes and rinsed in cold water. The time of immersion in the respective acids was dependent on the freshness and temperature of the acids.

The paper-phenolic laminate had a glossy smooth surface to which none of the glues adhered very well. Washing with soap and water or soaking in benzene or acetone did not affect this passive surface. The surface layer had to be entirely eliminated by sanding with No. 00 sandpaper (references 9, 10, and 11).

The glass was cleaned by heating in a sodium dichromate-sulfuric acid solution and rinsing thoroughly in water. The birch-wood and hard-rubber specimens were cleaned by sanding with No. 00 sandpaper (reference 12).

The solvent used for preserving the fresh surface depended upon the adhesive to be used, as follows:

Adhesive	Solvent used to preserve adherend surface
Cellulose nitrate	Ethyl acetate
Polyvinyl acetate	Acetone
Resorcinol-formaldehyde	Acetone
Casein	Acetone
Gum arabic	Acetone
Rubber	Benzene
Neoprene	Ethyl acetate

In the case of the resorcinol-formaldehyde, casein, and gum-arabic adhesives, which were used in aqueous solution, the adherend surface was air-dried 15 minutes before applying the adhesive. Although acetone is soluble in water, it is not a solvent for casein or gum arabic and tended to precipitate them from the aqueous solutions. The wood specimens were not immersed in a solvent; the surfaces of this adherend were sanded immediately prior to application of adhesive.

Procedure for Bonding Specimens

The clamping frames used in assembling the specimens are shown in figures 1 and 2. It was found that, to prepare the test specimens properly, different conditions for drying the coated adherends and bonding the assemblies were required with each adhesive. The time, temperature, and pressure conditions employed are shown in table II.

The temperature rise during the bonding cycle with the neoprene adhesive was determined with a thermocouple placed in the adhesive. It was found that 2 hours was required to reach the correct temperature. The prescribed time of cure at 120° C is 2.5 hours (reference 13). By adding 1 hour to the prescribed time to compensate for the temperature lag, a complete cure was obtained. The natural-rubber cement was cured for various lengths of time at 140° C until the curing time was found which would produce a properly vulcanized product.

For polyvinyl acetate, resorcinol-formaldehyde resin, casein, and gum arabic, all of which flow readily, a pressure of only 3 pounds per square inch was required to produce full contact between the coated surfaces. For cellulose nitrate and the natural- and synthetic-rubber adhesives, the resistance to flow was much greater and pressures of 150 to 200 pounds per square inch were necessary to insure close contact between the adherend surfaces in the assembly.

TEST PROCEDURES

All specimens were conditioned for a minimum period of 7 days at a temperature of 25° C and 50 percent relative humidity and were tested under these conditions. Two Baldwin-Southwark universal hydraulic testing machines of 2400- and 60,000-pound capacities, respectively, with scale ranges of 240, 1200, 2400, 12,000, and 60,000 pounds, were used to make the shear and tensile tests.

Shear Tests

Double-lap-joint specimens were used in determining shear strengths of the adhesive-adherend combinations. The specimens were broken under a tensile load except for glass bonded with cellulose nitrate and polyvinyl acetate. These latter specimens failed repeatedly in the adherend under tensile loading; compression loading gave more satisfactory results.

Sheet material of two thicknesses, approximately $1/8$ and $1/4$ inch, were used to make tensile-type shear specimens; the thicker strip was used between two of the thinner strips, as shown in figure 3(a). An exception to this was necessary in the case of the stainless steel which was available only in 0.1-inch thickness; three strips of equal thickness were used to make the shear specimens of this material. The strips were machined to 5- by 1-inch dimensions and bonded with an overlap of 1.0 inch. When failure occurred in the adherend, the overlap was reduced to 0.5 or 0.3 inch, as indicated in the tabulated data.

Templin type self-alining grips were used in the shear tests with tensile loading. The rate of loading was adjusted within the limits of 200 to 1000 pounds per minute so that the maximum load was applied in about 3 minutes. The loading rate for each system was determined by trial tests.

The compression-type shear specimens were made of strips of glass 1 inch long, 0.5 inch wide, and 0.25 inch thick, with an overlap of 0.3 inch (fig. 3(d)). They were tested in a subpress as shown in figure 4. Blotting paper was placed at the bearing surfaces of the glass to prevent stress concentration and premature failure of the test specimen. The rate of loading was adjusted as described for the tests with tensile-type shear specimens.

Tensile Tests

Tensile-adhesion strengths of the adhesive-adherend combinations were determined by using specimens and self-alining grips (fig. 5) described in reference 14.

The glass specimens (fig. 6(a)) were cast from melted 1-inch-thick plate glass. The specimens were machined from $1\frac{7}{8}$ -inch-diameter rod in the case of the two metals (fig. 6(b)) and from 1-inch-thick sheet in the case of the phenolic laminate, birch wood (fig. 6(c)), and hard rubber.

The contact area for the tensile specimens was 1 square inch except when smaller contact areas had to be used because the specimens failed in the adherend. A contact area of 0.25 square inch was used for the phenolic laminate bonded with cellulose nitrate, polyvinyl acetate, and casein; for glass bonded with cellulose nitrate and polyvinyl acetate; and for hard rubber bonded with cellulose nitrate (fig. 6(d)). A contact area of 0.5 square inch was used for all specimens prepared with the birch wood.

The rate of loading in the tensile tests was adjusted within the limits of 200 to 1000 pounds per minute so that the maximum load was applied in about 3 minutes.

Long-Time Loading Tests

The same type of double-lap-joint specimen used in the shear tests made with tensile loading was employed in the long-time loading tests (fig. 3(b)). An overlap of 0.5 inch was adopted and the strips were machined to widths selected to obtain average shear stresses of 200 to 1300 pounds per square inch. The load was applied by hanging either a 50- or a 100-pound weight from the specimen (fig. 7).

Impact Tests

Single-lap-joint specimens of aluminum alloy and wood were used to evaluate the impact strength of bonds made with the various types of adhesives. The specimens were made with strips 2.8 inches long and 0.5 inch wide with an overlap of 0.5 inch (fig. 3(c)). The thickness of the strips was 0.1 inch for the aluminum alloy and 0.25 inch for the wood. The specimens were tested both edgewise and flatwise by the Charpy impact method with a Baldwin-Southwark pendulum machine having a capacity of 2 foot-pounds (fig. 8).

RESULTS OF TESTS

Shear and Tensile-Adhesion Strength

The data obtained in the shear and tensile-adhesion strength tests are presented in tables III and IV, respectively. The data are grouped according to adhesives in figure 9 and according to adherends in figure 10.

Polyvinyl acetate adhesive gave consistently high tensile-adhesion and shear strengths with all adherends. With stainless steel and aluminum alloy the shear and tensile-adhesion strengths were 2900 to 3600 pounds per square inch. In only three instances, with wood and hard rubber in tensile adhesion and with hard rubber in shear, did the polyvinyl acetate fail to give the highest values.

Cellulose nitrate plasticized with camphor ranks next to vinyl acetate resin in giving strong bonds with all the adherends. However, it was necessary to use a large amount of the plasticizer to obtain fusible adhesive films.

The resorcinol-formaldehyde resin adhesive produced good bonds with the organic adherends and bonds of negligible strength with the inorganic substances.

Casein and gum arabic, which depend on loss of water to achieve their optimum strength, gave highest values with the absorbent materials such as wood and paper-phenolic laminate. Shear specimens of aluminum bonded with gum arabic showed an appreciable gain in strength when they were given a long conditioning and drying period (table III). They increased in strength from a value of 330 pounds per square inch for the usual 7-day period to 530 pounds per square inch for a 20-day drying period.

The rubber cements gave uniformly low values. Cure of the natural rubber to a hard nonrubbery texture gave higher values. For example, the tensile-adhesion value for wood bonded with overcured natural rubber was 530 pounds per square inch, compared with 174 pounds per square inch for a rubbery cure.

Good bonds were obtained with the metals and glass only with the polyvinyl acetate and cellulose nitrate adhesives.

Wood and paper-phenolic laminate were the only nonisotropic materials used. The load was applied in the strongest direction of these materials in the shear test and in the weakest direction in the tensile adhesion test. The large differences between the shear and tensile-adhesion strengths of these two materials were probably due to this factor (reference 9).

In quite a few of the tests the values were affected by the strength of the material bonded since the failures were wholly or partly in the adherends. However, the strength of the adherend is not the only determining factor in the failure of the bond. The wide spread in the strength values, obtained in tests in which a given adherend bonded with various adhesives showed cohesive failure, suggests that additional chemical or physical factors are involved.

For example, with paper-phenolic laminate, adherend failure occurred with shear specimens bonded with polyvinyl acetate, cellulose nitrate, resorcinol resin, and casein adhesives at average shear stresses of 2480, 1680, 1370, and 1030 pounds per square inch, respectively. The amount of adherend failure was 90 to 100 percent for the first three adhesives and averaged 35 percent for casein.

In a study of the effect of pH on the strength of wood veneers (reference 10) it was shown that acids and bases definitely weaken them. The casein formulation is very alkaline; when it was used with aluminum a large amount of corrosion was observed. This chemical action may be reflected in the values obtained with other adherends. Therefore, while chemical action between the resin and adherends such as paper-phenolic laminate or wood may strengthen the bond, it may also tend to weaken the wood or phenolic laminate.

The solvents which were used as the vehicles for cellulose nitrate and polyvinyl acetate could possibly have a weakening effect on the wood because of solvent action on the ligneous fiber-bonding material. Such activity may vary with the difference in penetrating powers due to differences in viscosities of the adhesive formulation.

Another physical factor capable of explaining variable strength values when adherend failure occurs is the ductility of the adhesive. The thermoplastic adhesives, by flowing at a yield stress, can relieve stress concentrations which exist at the ends of the laps in the shear specimen (reference 11).

Long-Time Loading Shear

The results of the long-time loading test are presented in table V. Figure 11 indicates clearly the difference in behavior of thermosetting and thermoplastic resin adhesives.

For the specimens bonded with polyvinyl acetate, the static test is an indication of the adherend strength since the speed of loading is greater than the plastic flow and the adhesion strength is greater than the adherend strength.

On the other hand, in the long-time loading tests with specimens bonded with polyvinyl acetate, plastic flow of the adhesive is the main cause of failure. The rate of plastic flow is such that from 600 to 2500 pounds per square inch the bonds fail in less than 4 hours. Below 600 pounds per square inch the plastic flow decreases rapidly so that a relatively small drop in stress greatly increases the time to failure.

Three wood specimens bonded with resorcinol resin were subjected to the long-time load test. Two of them broke under loads of 1360 and 1070 pounds per square inch in 65 and 219 hours, respectively. In

both cases the failure was partially in the wood. The third specimen supported a load of 680 pounds per square inch for 6 months, at which time the test was discontinued. Thus, plastic flow of the adhesive is not a major factor in the failure of wood joints bonded with the thermosetting resin.

Impact Strength

The results of the impact tests on single-lap-joint specimens are shown in table VI. The rubber adhesives which were relatively weak in the static strength tests were superior in resistance to impact. This behavior is most pronounced for the aluminum specimens. The average impact strength of the neoprene-bonded aluminum specimens for flatwise and edgewise testing was about 1 foot-pound compared with 0.17 foot-pound or less with polyvinyl acetate cement, a factor of 6 or more in favor of the neoprene adhesive. In contrast the tensile-adhesion and shear strength values for the neoprene with aluminum alloy are about a tenth of the values for specimens bonded with polyvinyl acetate.

Likewise, the wood impact specimens bonded with natural rubber and resorcinol adhesives had impact strengths of 0.6 and 0.4 foot-pound, respectively, in edgewise tests and 0.17 and 0.08 foot-pound, respectively, in flatwise tests. In the static tests with wood specimens the resorcinol resin adhesive was 2 to 10 times as strong as the rubber cement.

THEORETICAL ASPECTS

It is of interest to consider the results of these tests on the relative strengths of various adhesive-adherend combinations with respect to the nature of the interface. A knowledge of the physical and chemical nature of the surfaces involved is necessary to establish the type of bond formation which may occur (reference 8). Several types of bonds are recognized as factors in adhesion: (1) Electrostatic or polar bonds which are formed in the actual transfer of electrons from one atom to another, (2) covalent bonds which are the type encountered in diatomic elements and most organic compounds, (3) coordinate covalent bonds which are weaker than the true covalent type and are exemplified by hydrogen bridging, and (4) Van der Waal's forces which consist of molecular attractions operating over greater distances than those involved in the formation of primary valence bonds. Specific adhesive bonds may be attributed to any of the foregoing factors or to various combinations of them.

It might be expected that when secondary forces are involved the polarity of the materials at an interface would be a predominant factor

in the strength of the bond between them. It is known that the force between molecules with high dipole moments is greater than that between molecules with low or no dipole moments. The dielectric constant can be used as a relative measure of the polarity or dipole moment. Consequently, adhesive-adherend combinations in which the sum of the dielectric constants is high should have high strength provided that the interfacial surfaces are clean.

Measurements of the dielectric constants of specimens of the materials used in this project were made by the Inductance and Capacitance Section of the National Bureau of Standards. The resorcinol resin had an unexpectedly high dielectric constant for which no explanation is known (rechecked with second specimen). Dielectric-constant measurements of the metals were not possible because of their conducting nature. Metal structure is relatively homogeneous and nonpolar. However, because of its freely flowing electrons, a metal has mirror image forces induced at its surfaces which are equal and opposite to the polar forces in the adhesive used with it (reference 15). Therefore, insofar as polar properties are concerned, an adhesive should have as great an affinity for a metal as it would have for a material of like polarity.

Since all the adhesives were applied in a liquid or solution form, the dipoles present were free to orient themselves while setting, according to the influence of any forces present in the adherends. In table VII the double-lap shear strengths of the various adhesive-adherend combinations are shown with the adhesives and adherends arranged according to increasing dielectric constants. The double-lap shear strength values were used because for this type of specimen the strongest grain direction was used for wood and paper-phenolic laminate. These values would then be a closer approach to the actual bond strength since cohesive failures play a smaller role in this test. This table does not show that the polar forces involved played any dominating part in the adhesive strength. The higher adhesive strengths are not concentrated in the regions where the sums of the dielectric strengths are higher. Rather, the higher shear strengths are distributed over a wide range of dielectric constants.

When the values in the columns of table VII are averaged horizontally and vertically, four values stand out. These are the values for polyvinyl acetate and cellulose nitrate of the adhesives and for wood and paper-phenolic laminate of the adherends. Polyvinyl acetate has the highest value with five of the six adherends. If the bond strengths correlated with dielectric constant, the strengths of the combinations made with cellulose nitrate should be superior to those made with polyvinyl acetate. The average values for all combinations for these two adhesives are the reverse of that expected on this basis. The combinations with cellulose nitrate are second highest with four of the six adherends and first with hard rubber.

Except for the value of casein with birch wood, the values for the combinations of polyvinyl acetate and cellulose nitrate are

consistently higher with all the adherends than for any of the other adhesives. The reason for this can probably be found in their thermoplastic properties. These properties allow them to form an ideal bond, one which is bubble-free and strain-free and which retains enough flow to compensate for temperature differentials. Thus fuller use is made of the existing attractive forces since they are not modified so much by the mechanical factors involved in adhesion and testing as is the case with thermosetting adhesives.

Birch wood and paper-phenolic laminate, while not so strong as the metals, have consistently high values with a greater range of adhesives. This is illustrated in their higher over-all averages. Here again the respective polarities, as represented by the dielectric constants, do not seem to be the deciding factors. Neoprene with a fairly high dielectric constant has consistently low strength values with all the adherends. Birch wood and paper-phenolic laminate have properties which allow them to accommodate a wide range of adhesives. These two materials have a larger effective surface area and more attractive groups for the adhesives than the other adherends.

Adhesives had very poor adhesion to paper-phenolic laminate unless its surface was sanded. This sanding may tend to expose cellulose fibers similar to the wood fibers.

Since the rigidity of the materials may have a bearing on the results, the double-lap shear strengths of the various adhesive-adherend combinations are shown in table VIII with the adhesives and adherends arranged according to the moduli of elasticity in tension. For birch wood the modulus of elasticity varies from 80,000 pounds per square inch perpendicular to the grain to 2,000,000 pounds per square inch parallel to the grain. The modulus of elasticity of gum arabic could not be found in the literature but was assumed to be of the order of that of casein. The value for resorcinol resin was assumed to be similar to that for unfilled phenolic resin.

The values in table VIII seem to have a more definite correlation than those in table VII. Where the modulus values of both adhesive and adherend are low, the strength values are low. Combinations of high modulus materials also give low strength values. Combinations which include at least one material of medium modulus exhibit the highest strengths. Natural rubber and neoprene are soft materials and in testing assemblies containing them a concentration of stresses is produced at the bond between the soft, highly elongated rubber adhesive and the hard, slightly elongated adherend when low loads are applied. When both adhesive and adherend have high modulus values neither material flows sufficiently during the final stages of the bonding process to relieve the stresses developed when the adhesive layer shrinks on cooling (reference 16) and drying (reference 17). Resorcinol resin combinations with glass and the metals are good illustrations of the incompatibility of high-modulus materials.

Several metal-to-metal adhesives now available commercially make the best use of their inherent strong adhesive forces not by attempting to change the polarity but by adjusting the physical properties. These adhesives are sometimes known as mixed phenolic-elastomer type. The rigidity of the phenolic resin base is modified by the addition of rubberlike materials. The combination gives a compound with desired properties such as proper modulus of elasticity and heat resistance without affecting appreciably the attractive forces of the ingredients. The resulting adhesives are used to bond practically anything which can withstand the pressures and temperatures necessary for their application.

Strong bonds produced by adhesives at ordinary temperatures are not necessarily permanent under all conditions. Turner (reference 16) has shown that when the temperatures are reduced large stresses are produced with rigid materials which have different coefficients of thermal expansion. These stresses serve to counteract the attractive forces producing the bond. Rigid adhesives may be either thermosetting types or thermoplastic types below their "second-order transition points." Thermoplastic types above this transition temperature flow sufficiently to reduce markedly the stresses induced by thermal expansion action. Turner has also shown a method for formulation of plastic compositions to reduce the stresses for rigid materials by reducing the differences in coefficients of thermal expansion.

In this project the adhesive-adherend combinations were studied in the simplest possible form. The types of adhesives and adherends used covered a rather wide range. The attractive forces involved and the mechanical factors hindering adhesion also covered a wide range.

The problems involving a fundamental investigation of adhesion may be classified as follows: (1) Characteristics of the bond interfaces, (2) factors affecting contact such as cleanliness and wetting, and (3) effect of physical properties of the materials themselves. Some specific problems indicated as a result of this work are as follows: (1) A more detailed study of the polarity theory, (2) the mechanism of bond rupture, (3) methods for producing clean surfaces, (4) wetting characteristics, (5) effect of modulus of elasticity on strength measurements, and (6) effect of flow characteristics.

CONCLUSIONS

From an investigation of the strength properties of various adhesive-adherend combinations to determine some aspects of the nature of adhesion, the following conclusions can be drawn:

1. The tensile-adhesion and shear strengths for a given adhesive-adherend combination did not differ greatly except for wood and paper-phenolic laminate, which are nonisotropic.
2. The highest values for tensile-adhesion and shear strengths were obtained with polyvinyl acetate and cellulose nitrate adhesives. These two adhesives caused failure in the adherends except in the case of the two metals stainless steel and aluminum alloy. The strength values varied from 1360 to 3600 pounds per square inch with the metals and from 400 to 2480 pounds per square inch with the nonmetallic materials.
3. Resorcinol resin and casein gave strength values ranging from 590 to 1940 pounds per square inch with hard rubber, paper-phenolic laminate, and birch wood, materials of low to medium modulus. They have very little or no adhesion for glass and the metals.
4. Natural rubber, neoprene, and gum arabic adhered to all the adherends but the strength values were consistently low, ranging from 34 to 630 pounds per square inch.
5. Comparative long-time load tests demonstrated the superiority of a thermosetting adhesive over a thermoplastic adhesive for supporting structural loads. The resorcinol resin showed no appreciable flow in supporting a load of 680 pounds per square inch for 6 months without failure, whereas the polyvinyl acetate failed in 45 days under a load of 200 pounds per square inch.
6. The rubber-type adhesives which were weak compared with the other adhesives in the static load tests were definitely superior in the impact tests.
7. Better correlation of shear strengths was found with the moduli of elasticity than with the dielectric constants of the materials used in the various adhesive-adherend combinations.
8. Further investigation of the surface chemistry involved is needed to obtain a better understanding of the nature of adhesion. Furthermore, physical factors, such as modulus properties, thermal expansion, and flow characteristics, may modify or completely nullify the effect of attractive forces between adhesives and adherends.

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REFERENCES

1. Anon.: List of Publications on Glue and Plywood. Mimeo. No. 513, Forest Products Lab., U. S. Dept. Agriculture, Aug. 1944.
2. Dowling, Arthur P.: Wood Aircraft Assembly Glues. Modern Plastics, vol. 23, no. 1, Sept. 1945, pp. 156-158.
3. Gray, Basil P.: Adhesives - New Materials and Practices. Modern Plastics, vol. 22, no. 8, April 1945, pp. 126, 200.
4. Havens, G. G.: Metlbond - A Metal Adhesive for Aircraft. Mech. Eng., vol. 66, no. 11, Nov. 1944, pp. 713-714, 736.
5. Stephan, J. T.: Use of Glue in Aircraft Construction. Aviation, vol. 42, no. 3, March 1943, pp. 132-133, 311, 313, 315-316, 319-320.
6. McBain, J. W., et al.: Reports of the Adhesives Research Committee 1, 2, and 3. H. M. Stationery Office, London, 1922, 1926, and 1932.
7. Browne, F. L., and Brouse, D.: Nature of Adhesion between Glue and Wood. Ind. Eng. Chem., vol. 21, 1929, p. 74.
8. Rinker, R. C., and Kline, G. M.: Survey of Adhesives and Adhesion. NACA TN No. 989, 1945.
9. Anon.: Gluing of Paper-Base Phenolic Plastic. Rep. No. WD-11101, Boeing Airplane Co., Sept. 1943.
10. Anon.: Specification for Gluing Paper-Base Phenolic Plastic. Rep. No. WD-11102, Boeing Airplane Co., Oct. 1943.
11. Anon.: The Gluing of Laminated Paper Plastic (Papreg). Mimeo. No. 1348, Forest Products Lab., U. S. Dept. Agriculture, Jan. 1944.
12. Anon.: Effect of Sanding Birch and Maple Surfaces upon the Strength of the Glue Joint. Rep. No. W. E. 185-S-1, Curtiss Research Lab., Aug. 1943.
13. Anon.: Compounding and Processing of Neoprene Type GN. Rep. No. 42-2, E. I. du Pont de Nemours and Co., Inc., May 1944.
14. A.S.T.M. Committee D-14 on Adhesives: Tentative Method of Test for Tensile Properties of Adhesives. Aug. 28, 1944.
15. Brunauer, S.: The Adsorption of Gases and Vapors. Vol. I, Physical Adsorption. Princeton Univ., Princeton, N. J., 1943.

16. Turner, P. S.: The Problem of Thermal-Expansion Stresses in Reinforced Plastics. NACA ARR, June 1942.
17. Turner, Phillip S., Doran, Jewel, and Reinhart, Frank W.: Fairing Compositions for Aircraft Surfaces. NACA TN No. 958, 1944.

TABLE I.- DESCRIPTION OF ADHERENDS

Adherend	Type	Manufacturer	Nominal thickness of sheet (in.)
Stainless steel	18-8	Allegheny Ludlum Steel Corporation	.10 al.87
Aluminum alloy	24S-T	Aluminum Company of America	.10 .20 al.87
Paper-phenolic laminate	Grade X	Westinghouse Electric Company	.10 .20 1.00
Glass	Plate	Pittsburgh Plate Glass Company	.125 .25 1.00
Wood	Yellow birch	Parkwood Corporation	.125 .25 1.00
Hard rubber	-----	American Hard Rubber Company	.10 .20 1.00

Diameter of rod.



TABLE II.- DESCRIPTION OF ADHESIVES AND PROCESSING DATA

Adhesive	Type	Manufacturer	Formulation (parts by wt.)	Drying conditions			Bonding conditions		
				Time (hr)	Temperature (°C)	Time (hr)	Temperature (°C)	Pressure (lb/sq in.)	
Cellulose nitrate	20-sec viscosity	Hercules Powder Co.	Cellulose nitrate Ethyl acetate Camphor	10 85 5	25	2	120	150-200	
Polyvinyl acetate	AYAF	Carbide and Carbon Chemicals Corp.	Polyvinyl acetate Acetone	20 80	50 80	2	120	3	
Resorcinol resin	Penacolite Gil31	Pennsylvania Coal Products Co.	Resorcinol resin Catalyst	5 1	25	20	65	3	
Casein	Reg. B 1	Casein Company of America	Casein Water (soak for 15 min) Calcium hydroxide Sodium fluoride Sodium phosphate (12 H ₂ O)	100 300 30 5.8 17.4	25	20	25	3	
Gum arabic	GU 2	Arabul Manufacturing Co.	Gum arabic Water Thymol	50 50 2.5	25	20	25	3	
Rubber	Smoked sheet	-----	Rubber Benzene Zinc oxide Sulfur	100 400 5 4	25	7	140	150-200	
Neoprene	CN	E. I. du Pont de Nemours and Co., Inc.	Neoprene Ethyl acetate Zinc oxide Magnesium oxide	100 200 5 4	25	3.5	120	150-200	



TABLE III.- SHEAR STRENGTH DATA FOR VARIOUS ADHESIVE-ADHEND COMBINATIONS^a

Adherent	Adhesive	Cellulose nitrate	Polyvinyl acetate	Resorcinol resin	Casein	Gum arabic	Rubber	Neoprene
Stainless steel								
Shear strength (lb/sq in.)		1580	2960	0	190	130	270	90
Standard error (lb/sq in.)		29	44	-----	29	16	18	4.5
Coefficient of variation		6.2	5.2	-----	55	30	20	17
Number of specimens		11	12	-----	12	6	9	11
Aluminum alloy								
Shear strength (lb/sq in.)		1360	3560	0	120	b330	250	130
Standard error (lb/sq in.)		32	65	-----	12	b22	15	21
Coefficient of variation		8.0	8.8	-----	28	b50	18	53
Number of specimens		12	23	-----	8	b10	9	11
Paper-phenolic laminate								
Shear strength (lb/sq in.)		cd1680	ce2480	ce1370	cl030	440	130	250
Standard error (lb/sq in.)		31	93	28	30	24	5.5	6
Coefficient of variation		6.4	12	6.8	10	18	15	8.2
Number of specimens		12	10	11	12	11	12	12
Glass								
Shear strength (lb/sq in.)		cdf1680	cdf2310	0	29	210	43	100
Standard error (lb/sq in.)		42	110	-----	6	7.1	3.5	14
Coefficient of variation		9.5	11	-----	55	10	28	48
Number of specimens		14	6	-----	8	9	12	11
Birch wood								
Shear strength (lb/sq in.)		cl390	ce1990	ce1940	ce1660	630	160	180
Standard error (lb/sq in.)		39	66	46	55	24	12	4.6
Coefficient of variation		9.3	10	9.7	11	13	26	8.9
Number of specimens		11	10	17	12	11	12	12
Hard rubber								
Shear strength (lb/sq in.)		cd1000	ce630	ce990	150	240	190	230
Standard error (lb/sq in.)		18	44	61	9.6	13	7	8.9
Coefficient of variation		6.3	22	23	21	18	13	13
Number of specimens		12	10	5	12	12	12	12

^aA double-lap tensile-type specimen with an overlap of 1 inch was used unless otherwise noted.^bSpecimens dried for 20 days instead of 7 days gave the following results: shear strength (lb/sq in.), 530;

standard error (lb/sq in.), 68; coefficient of variation (percent), 43; and number of specimens, 11.

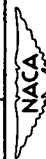
^cSpecimens failed partly in adherend.^dOverlap 0.4 inch or less.^eOverlap 0.5 inch.^fCompression shear.

TABLE IV.- TENSILE-ADHESION STRENGTH DATA FOR VARIOUS ADHESIVE-ADHEREND COMBINATIONS^a

Adherend	Adhesive	Cellulose nitrate	Polyvinyl acetate	Resorcinol resin	Casein	Gum arabic	Rubber	Neoprene
Stainless steel. Tensile adhesion strength (lb/sq in.) Standard error (lb/sq in.) Coefficient of variation (percent) Number of specimens		2180	3600	0	510	110	260	170
		66	72	-----	31	6	17	9
		10	10	-----	21	19	23	16
		12	25	25	12	11	12	9
Aluminum alloy Tensile adhesion strength (lb/sq in.) Standard error (lb/sq in.) Coefficient of variation (percent) Number of specimens		1500	3270	0	110	110	390	290
		100	59	-----	9.5	7	26	9
		23	9	-----	30	18	23	10
		12	25	17	12	9	12	12
Paper-phenolic laminate Tensile adhesion strength (lb/sq in.) Standard error (lb/sq in.) Coefficient of variation (percent) Number of specimens		bc860	bc1060	b830	bc690	630	160	170
		110	75	52	37	42	15	9
		40	23	19	18	21	31	17
		10	10	9	11	10	10	12
Glass Tensile adhesion strength (lb/sq in.) Standard error (lb/sq in.) Coefficient of variation (percent) Number of specimens		bc1040	bc2430	0	0	260	34	90
		230	170	-----	-----	17	5	12
		60	16	-----	-----	21	47	46
		7	5	13	6	10	10	11
Birch wood Tensile adhesion strength (lb/sq in.) Standard error (lb/sq in.) Coefficient of variation (percent) Number of specimens		bd1100	bd960	bd1180	bd1020	d400	d170	d340
		66	39	42	16	15	45	13
		19	14	14	5.3	12	26	12
		10	12	16	8	9	9	10
Hard rubber Tensile adhesion strength (lb/sq in.) Standard error (lb/sq in.) Coefficient of variation (percent) Number of specimens		c590	400	b1340	130	320	130	240
		50	26	50	4	32	18	7
		27	20	12	11	31	44	12
		10	9	10	10	10	10	18

^aA specimen with a contact area of 1 square inch was used unless otherwise noted.^bSpecimens failed partly in adherend.^cContact area 0.25 square inch.^dContact area 0.5 square inch.

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TABLE V.- LONG-TIME LOADING SHEAR DATA FOR VARIOUS
ADHESIVE-ADHEREND COMBINATIONS^a

Adherend	Adhesive	Width (in.)	Overlap (in.)	Stress (lb/sq in.)	Time to failure (hr)
Paper-phenolic laminates	Polyvinyl acetate	1.00	0.50	2480	Static test ^b
		.075	.51	660	2 $\frac{1}{2}$
		.102	.51	480	36
		.220	.50	230	1080
Birch wood	Polyvinyl acetate	.98	.52	1990	Static test ^b
		.069	.52	1600	1/20
		.102	.52	1070	2
		.102	.52	1070	2 $\frac{1}{4}$
		.067	.50	750	2 $\frac{1}{6}$
		.160	.52	660	4
		.106	.51	500	168
		.12	.48	460	48
		.100	.55	450	30
		.162	.52	300	13
Birch wood	Resorcinol resin	.99	.52	1940	Static test ^b
		.081	.51	1360	b ⁶⁵
		.102	.51	1070	b ²¹⁹
		.077	.48	680	4320 (6 mo) without failure

^aA double-lap tensile-type specimen was used.

^bPartial failure in adherend.



TABLE VI.- IMPACT STRENGTH DATA FOR ADHESIVE-ADHEREND COMBINATIONS

[W_0 , capacity of that range of machine being used; W_a , indicated energy to break specimen, i.e., not corrected for friction and windage losses; W_b , energy to break specimen, i.e., W_a corrected for friction and windage losses; W_c , tossing energy, corrected for friction and windage losses;

W_d , tossing energy correction which is assumed to be as follows: $W_d = W_c \frac{W_0 - W_a}{W_0}$; $W_e = W_b - W_d$]

Adherend	Adhesive	Energy to break specimens, W_b (ft-lb)	Wood failure (percent)	Tossing energy, W_c (ft-lb)	Tossing-energy correction, W_d (ft-lb)	Impact strength, W_e (ft-lb)
Edgewise impact tests						
Birch wood	Polyvinyl acetate	0.241	0	0.040	0.034	0.207
	Resorcinol resin	.428	50	.040	.031	.397
	Gum arabic	.152	0	.044	.040	.112
	Rubber	.618	80	.042	.028	.590
Aluminum alloy	Polyvinyl acetate	.210	0	.041	.036	.174
	Neoprene	.985	0	.042	.021	.964
Flatwise impact tests						
Birch wood	Polyvinyl acetate	0.163	3	0.041	0.037	0.126
	Resorcinol resin	.116	65	.040	.037	.079
	Gum arabic	.065	0	.044	.042	.023
	Rubber	.208	45	.042	.037	.171
Aluminum alloy	Polyvinyl acetate	.106	0	.043	.040	.066
	Neoprene	.056	0	.045	.021	1.035



TABLE VII.-- VARIATION OF DOUBLE-LAP SHEAR STRENGTH VALUES WITH DIELECTRIC CONSTANTS OF ADHESIVES AND ADHERENDS^{a,b}

Adherend Adhesive	Hard rubber 2.91 (lb/sq in.)	Stainless steel (lb/sq in.)	Aluminum alloy (lb/sq in.)	Birch wood 5.2 (lb/sq in.)	Stainless steel (lb/sq in.)	Aluminum alloy (lb/sq in.)	Glass 7.74 (lb/sq in.)	Paper- phenolic laminates 9.14 (lb/sq in.)	Stainless steel (lb/sq in.)	Aluminum alloy (lb/sq in.)	Average (lb/sq in.)
Natural rubber 3.10	190	270	250	160			43	130			170
Polyvinyl acetate 3.61	630	2960	3560	1990			2310	2480			2320
Cellulose nitrate 5.9	1000			1390	1580	1360	1680	1680			1450
Casein 7.18	150			1660	190	120	29	1030			530
Neoprene 10.42	230			180			100	250	90	130	160
Gum arabic 16.1	240			630			210	440	130	330	330
Resorcinol resin 450-480	590			1940			0	1370	0	0	650
Average	430			1140			680	1050	6750	9820	

^aValues under materials are their dielectric constants.^bBecause metals have mirror image forces induced at their surfaces which are equal and opposite to polar forces of adhesives, stainless steel and aluminum alloy are distributed horizontally in accordance with dielectric constants of adhesives used with them.^cAverage shear strength value for all adhesives with this metal.

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TABLE VIII.— VARIATION OF DOUBLE-LAP SHEAR STRENGTH VALUES WITH

MODULI OF ELASTICITY OF ADHESIVES AND ADHERENDS^a

Adherend Adhesive	Hard rubber 500,000 (lb/sq in.)	Birch wood 80,000 to 2,000,000 (lb/sq in.)	Paper- phenolic laminates 2,100,000 (lb/sq in.)	Glass 10,000,000 (lb/sq in.)	Aluminum alloy 10,000,000 (lb/sq in.)	Stainless steel 25,000,000 (lb/sq in.)	Average (lb/sq in.)
Natural rubber 250	190	160	130	43	250	270	170
Neoprene 250	230	180	250	100	130	90	160
Cellulose nitrate 200,000-400,000	1000	1390	1680	1680	1360	1580	1450
Polyvinyl acetate 350,000-400,000	630	1990	2480	2310	3560	2960	2320
Gum arabic	240	630	440	210	330	130	330
Casein 540,000	150	1660	1030	29	120	190	530
Resorcinol resin 700,000-1,000,000	590	1940	1370	0	0	0	650
Average	430	1140	1050	620	820	750	

^aValues underneath materials are their moduli of elasticity in pounds per square inch.

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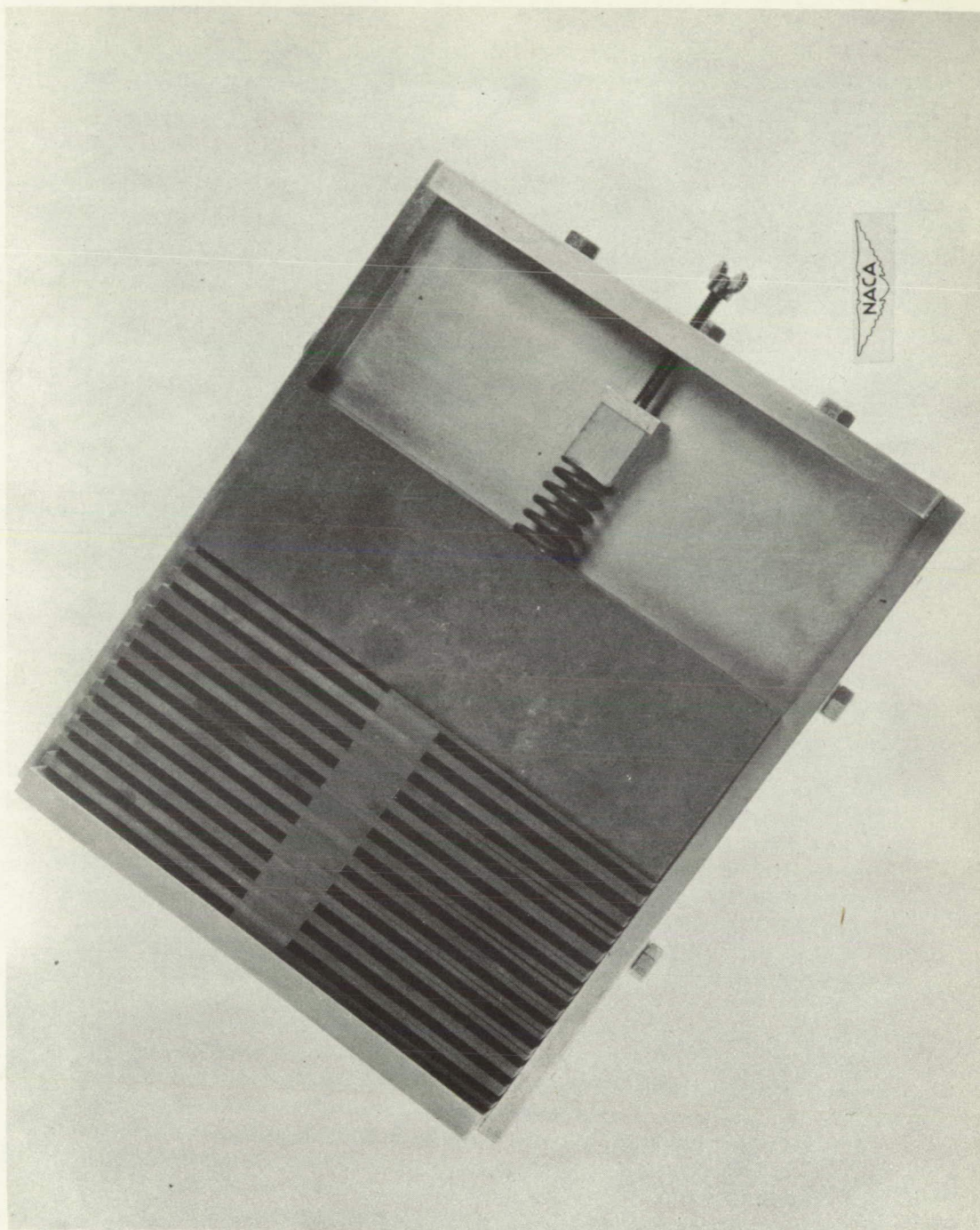


Figure 1.- Clamping frame for preparation of shear specimens.

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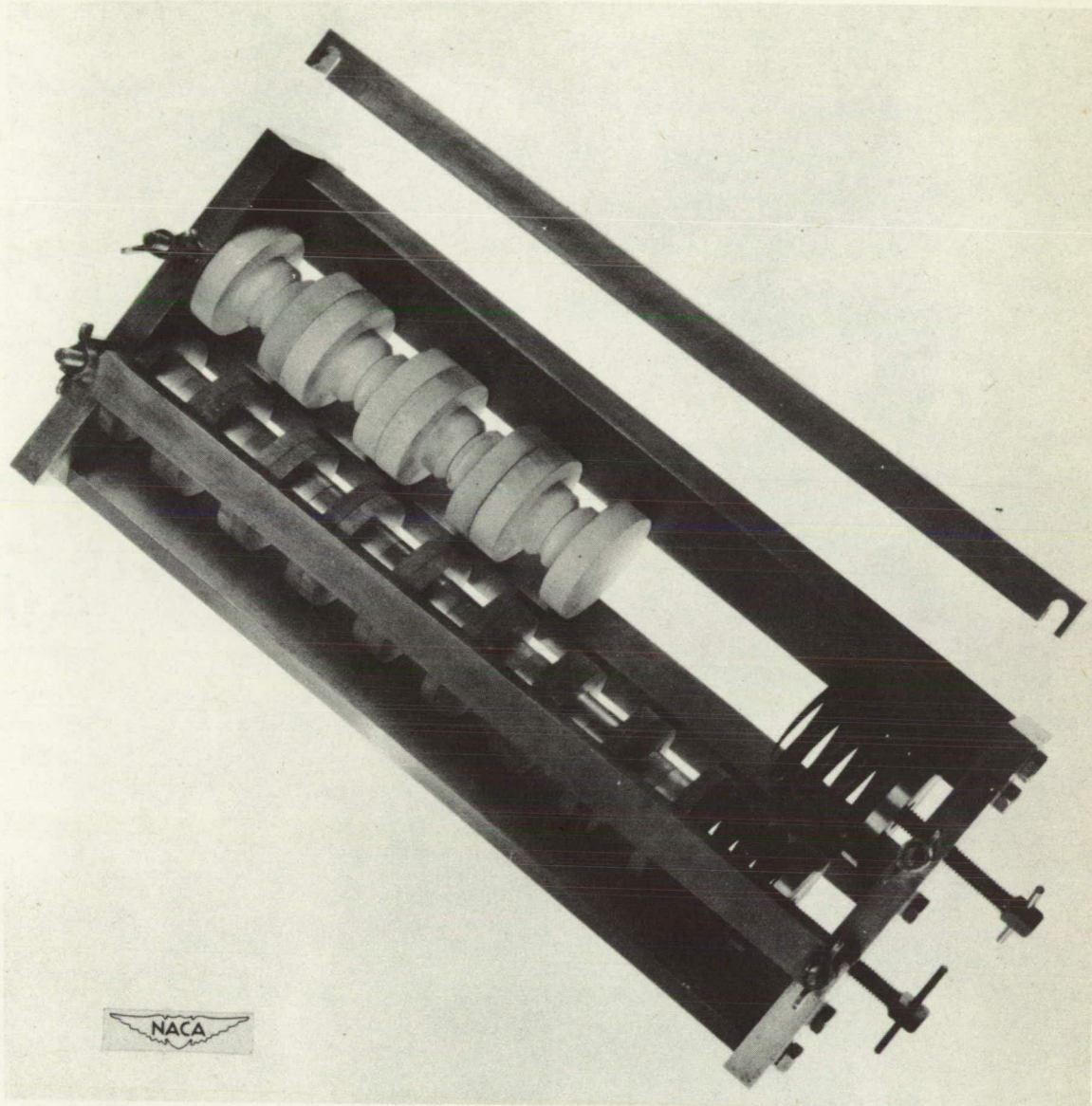


Figure 2.- Clamping frame for preparation of tensile specimens.

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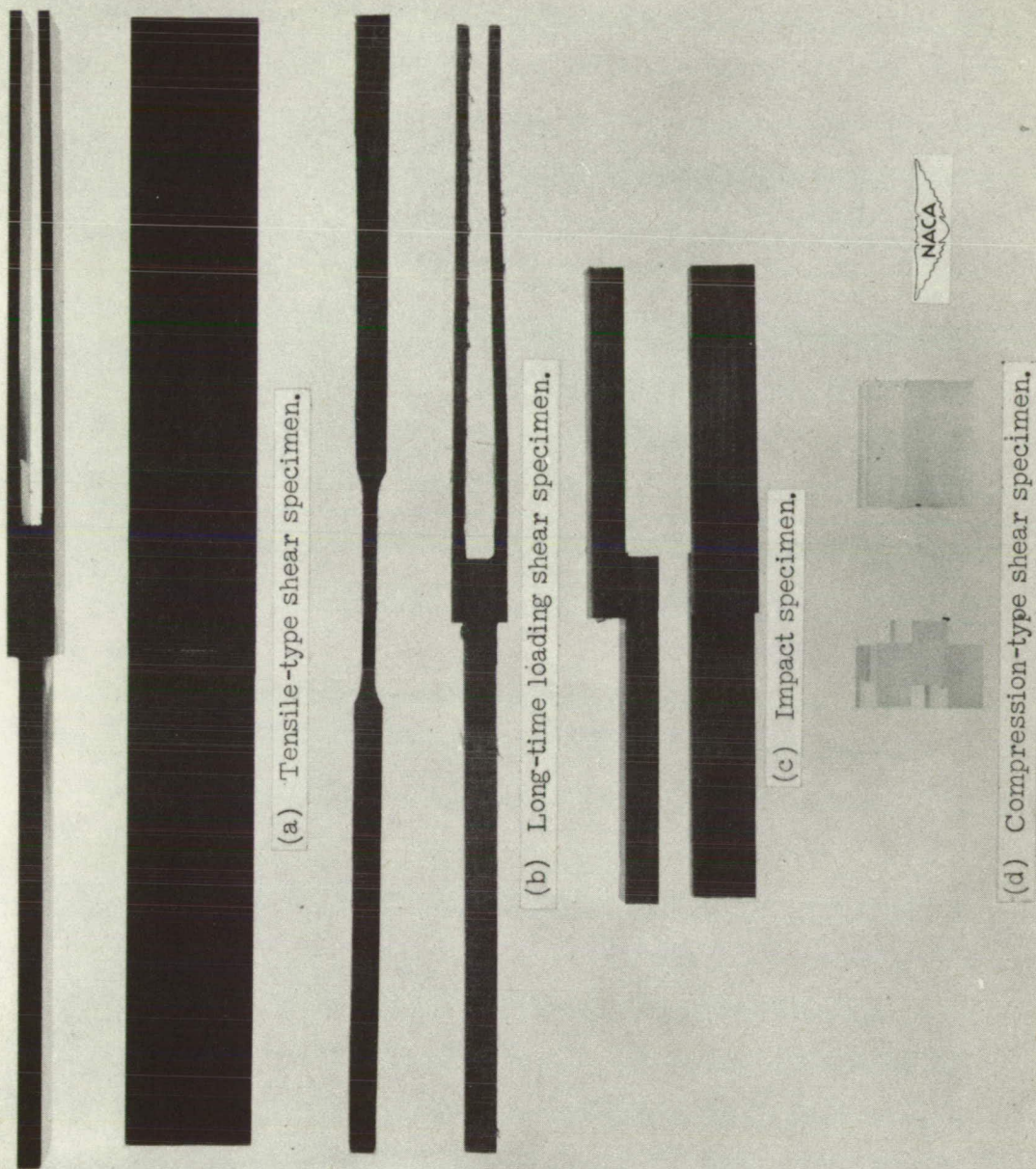


Figure 3.- Specimens for determination of shear and impact strengths.

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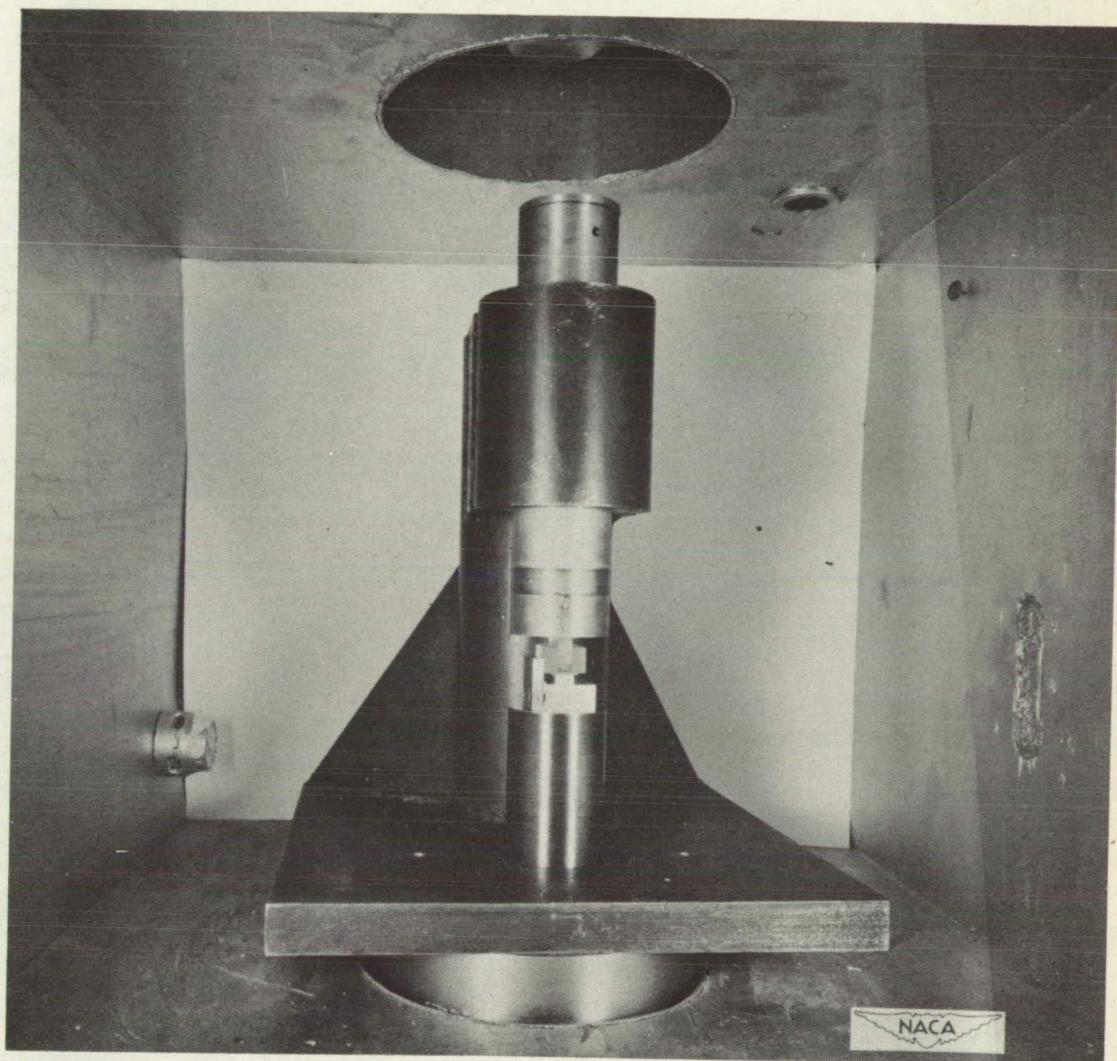


Figure 4.- Subpress for use in making compression-type shear test.

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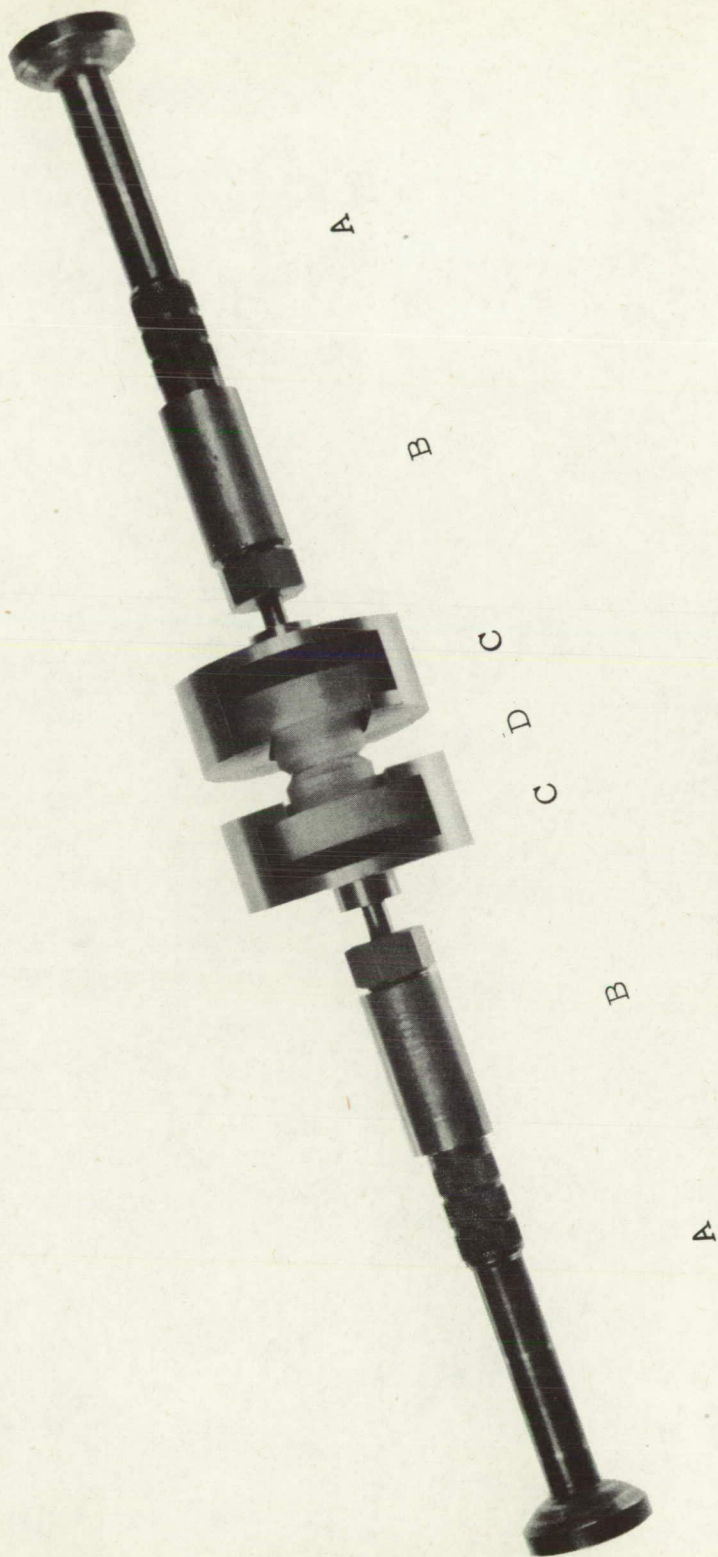


Figure 5.- Self-aligning grips used in making tensile-type shear test.

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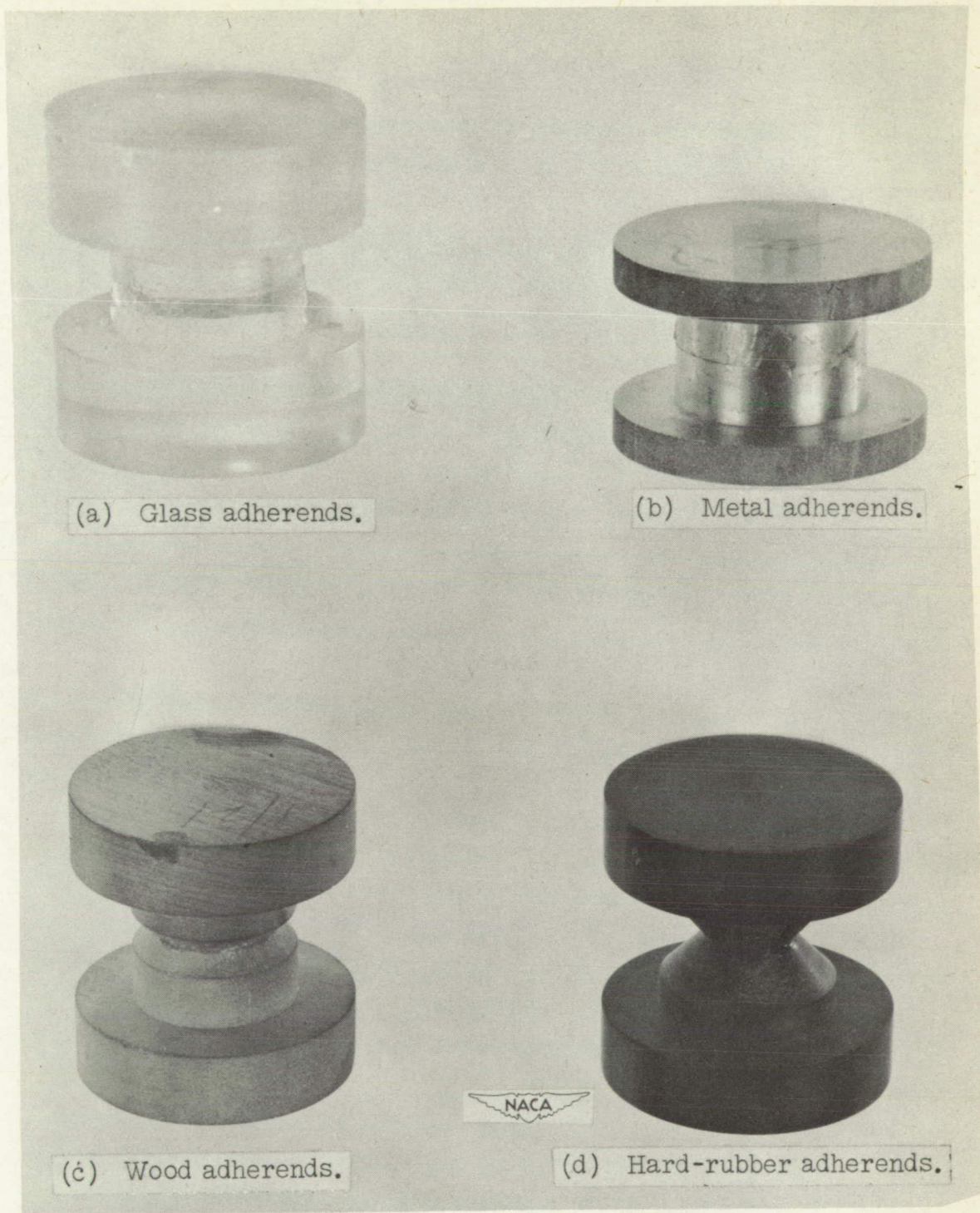


Figure 6.- Specimens for tensile-type shear test.

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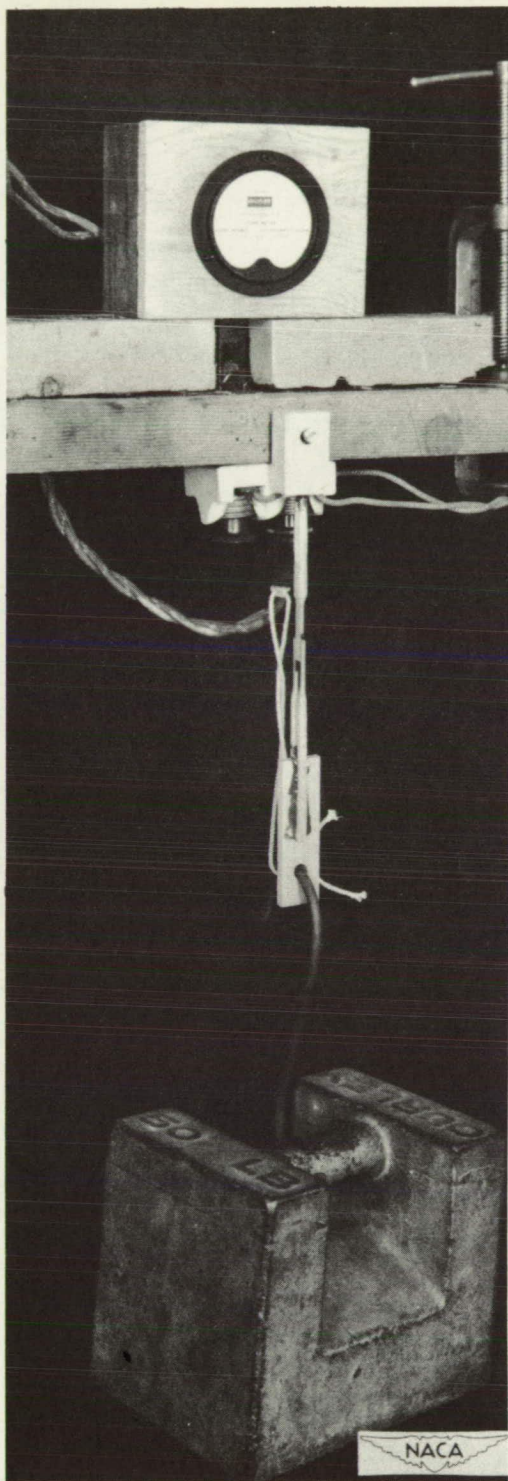


Figure 7.- Equipment used in making long-time loading test.

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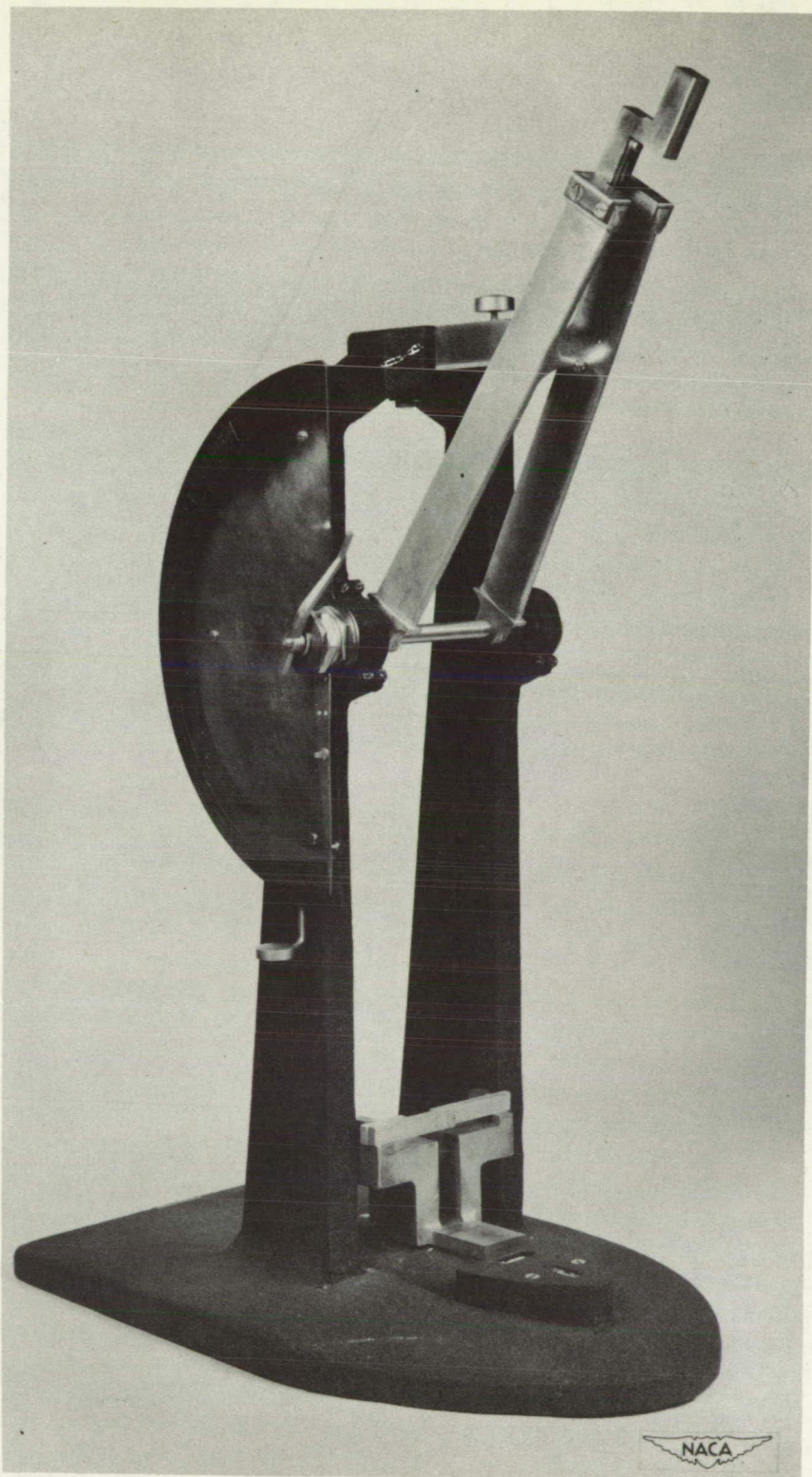


Figure 8.- Machine used in making Charpy impact test.

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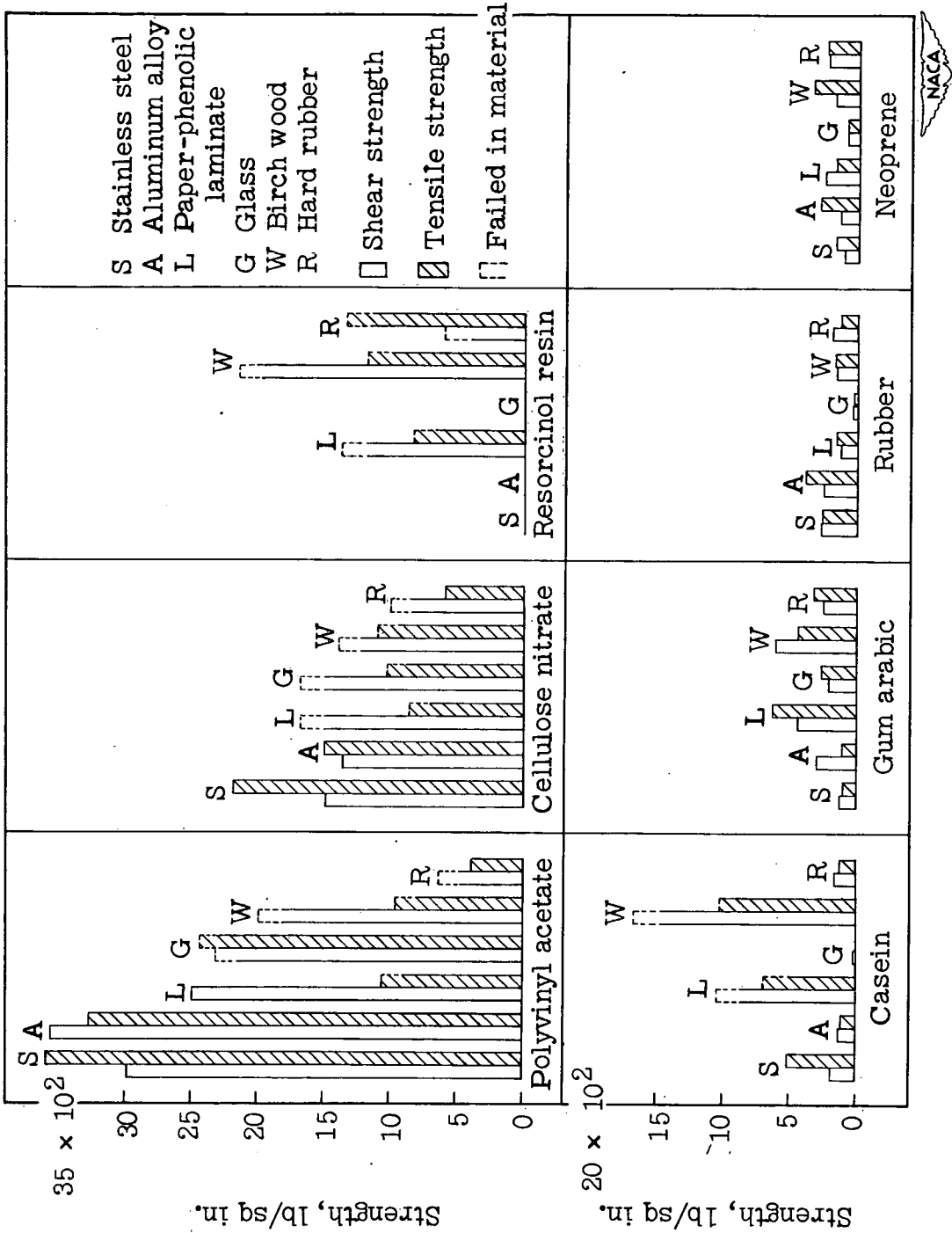


Figure 9.- Comparative bond strength values grouped according to adhesives used.

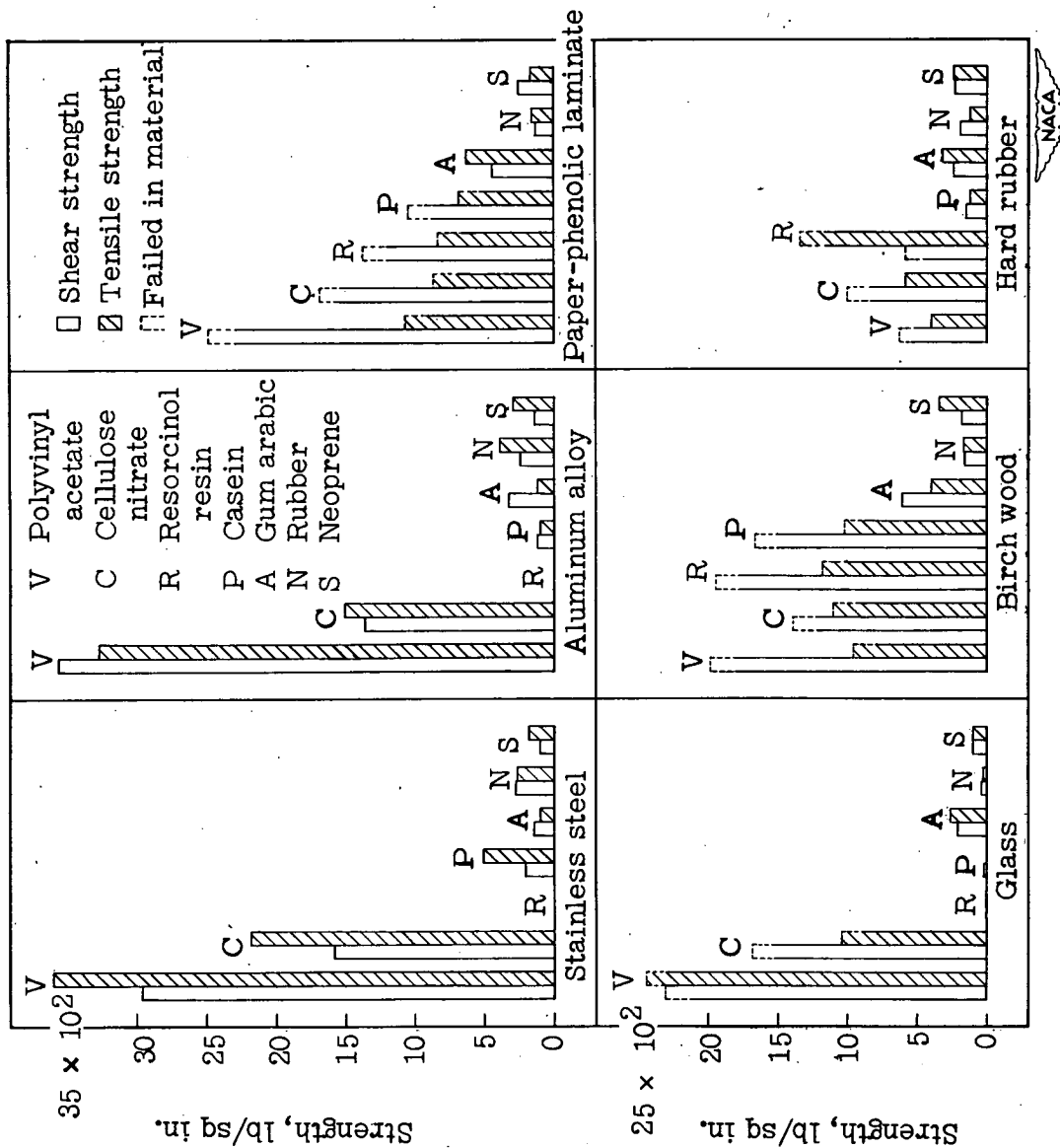


Figure 10.- Comparative bond strength values grouped according to adherends used.

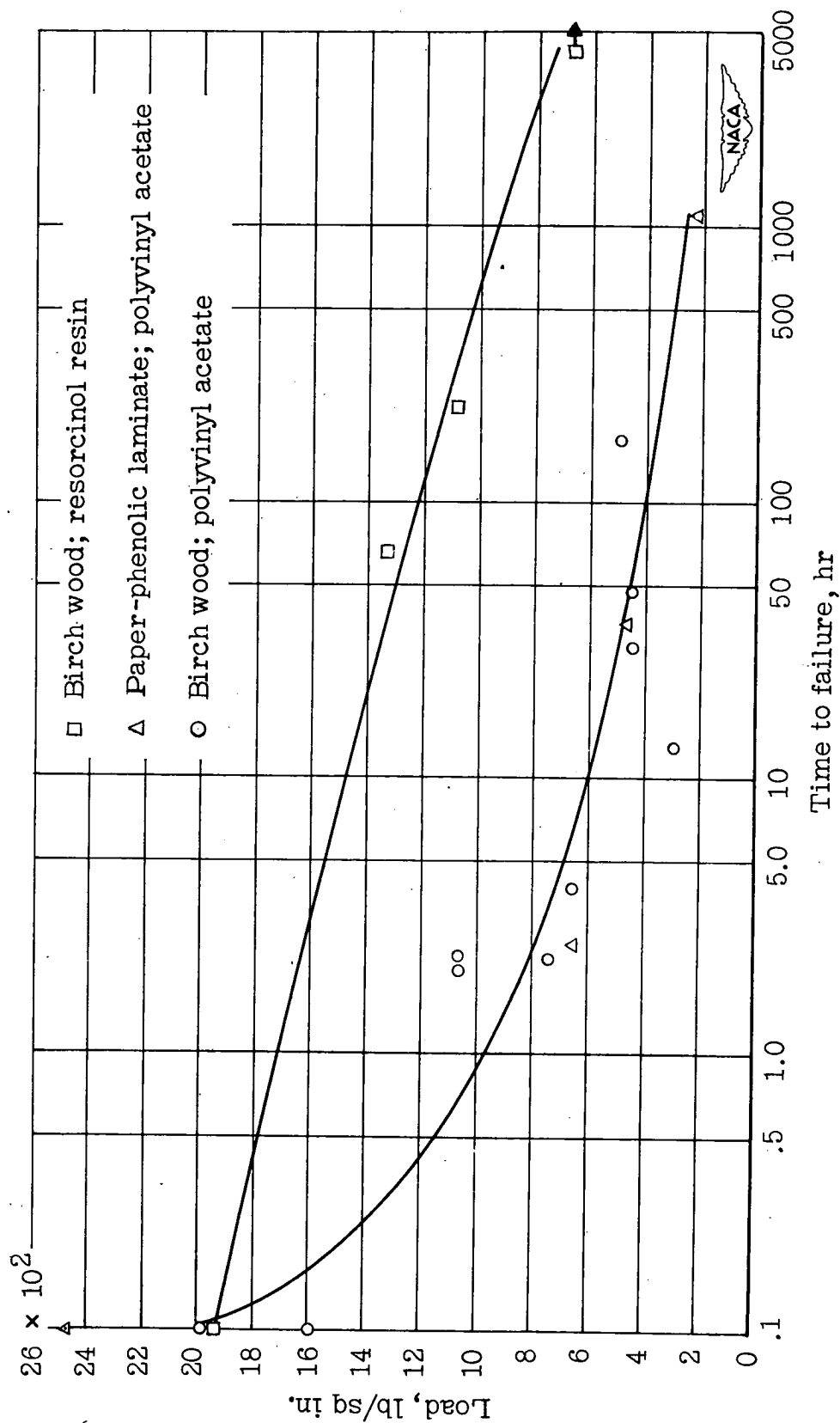


Figure 11.- Effect of long-time shear load on thermoplastic (polyvinyl acetate) and thermosetting (resorcinol resin) adhesive.